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Planar thermoelectric generator based on metal-oxide nanowires for powering autonomous microsystems

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Abstract

A planar ThermoElectric Generator (TEG) containing five thermocouples based on nanostructured metal-oxide elements wired electrically in series and thermally in parallel has been designed and fabricated. The thermoelectric elements consist of ZnO (*n*-type) and CuO (*p*-type) bundles of quasi-monodimensional nanowires deposited utilizing shadow masks. The TEG has been experimentally characterized, confirming feasibility of fabricating planar thermoelectric devices based on metal-oxide nanowires with the future aim to powering portable electronics and autonomous sensors and microsystems.

Keywords: Nanowires, Zinc Oxide, Copper Oxide, Seebeck Effect, Energy Harvesting, Thermoelectrics

1. Introduction

The efficiency of thermoelectric devices depends on the figure of merit *ZT*, which is related, among other parameters, to the Seebeck coefficient of the materials. The *ZT* of the best bulk materials is about 1 [1]. Recently, it has been demonstrated that Si-based quasi-monodimensional nanowires can be designed to achieve extremely large enhancements in thermoelectric efficiency, although at low temperature (T < 80 °C) [2-4]. Quasi-monodimensional metal-oxide nanowires would indeed be promising candidates to develop high efficiency thermoelectric devices due to their reduced dimensionality and excellent durability at high temperatures [5-6]. The Seebeck effect in ZnO [7] and CuO nanowires bundles

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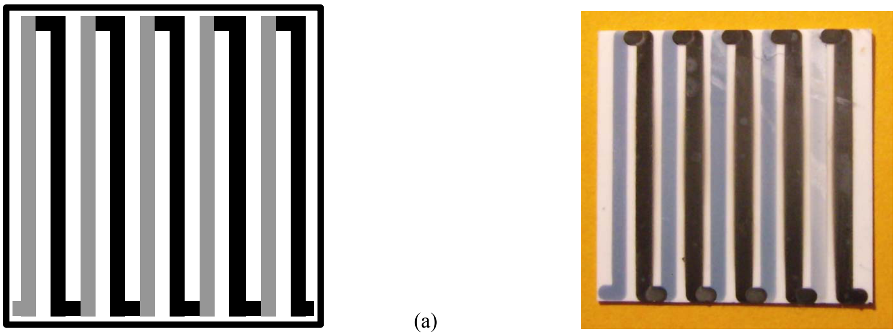
deposited by physical thermal processes has been previously investigated successfully measuring high thermoelectric coefficients.

2. Design and fabrication of planar thermoelectric generator

The fabrication of a thermoelectric generator requires both *n*- and *p*-type materials. Combining ZnO (*n*-type) and CuO (*p*-type) nanostructured elements, a planar thermoelectric generator, consisting of five thermocouples electrically connected in series and thermally in parallel, has been designed and fabricated. Thermoelectric materials have been deposited on alumina 20 mm x 20 mm substrates using shadow masks. Each element consists of an *S*-shaped strip with 20 mm length and 1 mm width. The electrical contact is given by overlap of adjacent strips. Figure 1 shows the layout and a top-view picture of the fabricated planar thermoelectric generator.



(a) (b)

Fig. 1. (a) Schematic layout and (b) top-view picture of the fabricated planar thermogenerator based on ZnO (grey) and CuO (black) nanostructured elements.

ZnO and CuO nanowires have been grown by a thermal evaporation process [8] and thermal oxidation technique [9], respectively. Gold nanoparticles have been deposited on alumina substrates by RF-sputtering as catalyst for ZnO nanowires growth. ZnO nanowires have been grown in a furnace before deposition of copper film, to avoid any contamination. For ZnO, deposition time has been set at 10 min, powder temperature at 1370 °C and substrate temperature at 800 °C, and the pressure inside the tube at 100 mbar, with 100 sccm argon flow. Copper film has been deposited by RF-sputtering (thickness 2 µm, room temperature, 5×10^{-3} mbar pressure, 50 W argon plasma). Then, the samples have been placed into a furnace and oxidized at 400 °C for 12 hours in 80 % oxygen - 20 % argon atmosphere (300 sccm flow).

3. Experimental characterization and discussion

The thermoelectric response of the fabricated thermoelectric generators has been experimentally investigated by means of a purposely developed experimental set-up, including two Peltier cells with driver stages as heaters, providing the temperatures T_A and T_B at the edges of the TEG, two reference Pt100 temperature sensors and a PC-based acquisition system, as shown in Figure 2. With the assumption that the temperatures T_A and T_B are uniform over each Peltier cell, the temperature difference ΔT applied across the sample has been calculated from measured data T_A and T_B, as:

$$\Delta T = T_A - T_B \qquad (1)$$

The thermoelectric voltages generated by single nanowire strips and the entire TEG have been measured

using a pair of copper probing tips as a function of the applied temperature difference ΔT and amplified by means of a low-noise instrumentation amplifier INA111 with a gain of 100.

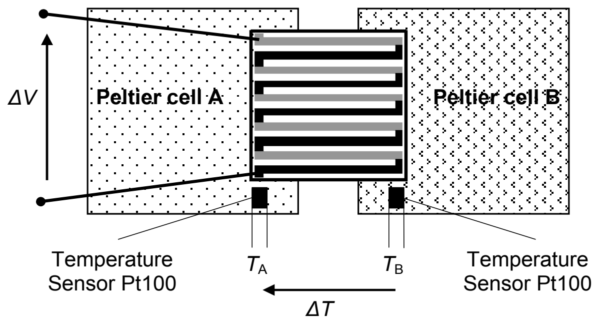


Fig. 2. Schematic diagram of the experimental set-up for the characterization of the fabricated thermoelectric generator.

The voltages ΔV_{ZnO} and ΔV_{CuO}, provided, respectively, by single ZnO and CuO strips, are reported in Figures 3.a and 3.b, together with the applied temperature difference ΔT as a function of the time. The thermoelectric coefficients α_{ZnO} and α_{CuO} of the ZnO and CuO strips have been estimated by linear fitting of the experimental data and they result in about -0.3 mV/°C and 0.5 mV/°C respectively. The sign of the measured thermoelectric coefficients is negative (positive) for ZnO (CuO) as expected for *n*-type (*p*-type) semiconductors [1].

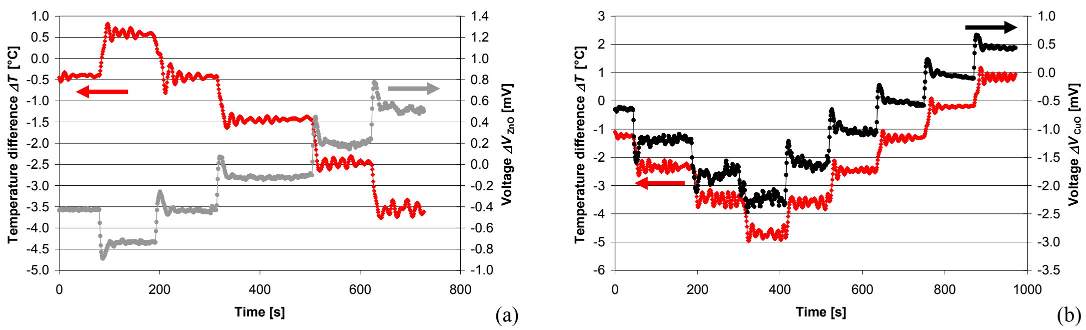


Fig. 3. Applied temperature difference ΔT and measured thermoelectric voltages ΔV_{ZnO} and ΔV_{CuO} versus time for (a) ZnO and (b) CuO nanowires strips.

The overall thermoelectric voltage ΔV, provided by the entire thermoelectric generator, is proportional to the applied temperature difference ΔT and the Seebeck coefficient S of the entire thermoelectric generator, as expressed by:

$$\Delta V = S\Delta T = N\alpha_{CuO,ZnO}\Delta T = N\left(\alpha_{CuO} - \alpha_{ZnO}\right)\Delta T \tag{2}$$

where $N = 5$ and $\alpha_{CuO,ZnO}$ are the number and the Seebeck coefficient of the ZnO-CuO thermocouples composing the thermoelectric device, respectively.

Figure 4.a shows the trends of the applied temperature difference ΔT and the thermoelectric voltage ΔV as a function of time. The thermoelectric coefficient S of the entire generator, estimated by linear fitting of measured data in Figure 4.b as predicted by (2), results of about 4 mV/°C, therefore each nanostructured ZnO-CuO thermocouple exhibits a Seebeck coefficient of about 0.8 mV/°C, as expected. The electrical

resistance of the entire TEG is about 9 MΩ.

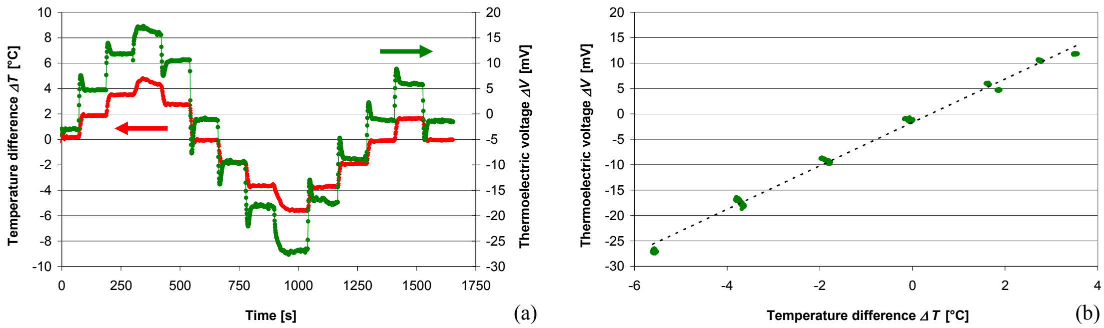


Fig. 4. (a) Applied temperature difference ΔT and the thermoelectric voltage ΔV versus the time and (b) the generated voltage ΔV versus the applied temperature difference ΔT for the entire thermoelectric generator.

4. Conclusions

A planar thermoelectric device based on five ZnO-CuO nanostructured thermocouples has been fabricated and investigated for power generation. Each thermocouple exhibits a Seebeck coefficient $\alpha_{\mathrm{Cuo,ZnO}}$ of about 0.8 mV/°C and the entire thermoelectric generator shows a thermoelectric coefficient S of about 4 mV/°C. Experimental data confirm the feasibility of fabricating planar thermoelectric generators for power generation based on ZnO and CuO nanowires deposited via shadow masks.

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References

[1] G.S. Nolas, J. Sharp, H.J. Goldsmid, *Thermoelectrics Basic Principles and New Materials Developments*, Springer, 2001

[2] P. Pichanusakorn, P. Bandaru, *Nanostructured thermoelectrics*, Materials Science and Engineering, 67, 2-4, (2010), 19-63.

[3] Z. Aksamija, I. Knezevic, *Thermoelectric properties of silicon nanostructures*, Journal of Computational Electronics, 9, 3-4, (2010), 173-179.

[4] C. J. Vineis, A. Shakouri, A. Majumdar, M. G. Kanatzidis, *Nanostructured thermoelectrics: big efficiency gains from small features*, Advanced Materials, 22, 36, (2010), 3970–3980.

[5] C.-H. Lee, G.-C. Yi, Y. M. Zuev, P. Kim, *Thermoelectric power measurements of wide band gap semiconducting nanowires*, Applied Physics Letters, 94, 022106 (2009).

[6] A. Vomiero, I. Concina, E. Comini, C. Soldano, M. Ferroni, G. Faglia, G. Sberveglieri, *One-dimensional nanostructured oxides for thermoelectric applications and excitonic solar cells*, Nano Energy, 1, 3, (2012), 372-390.

[7] S. Dalola, G. Faglia, E. Comini, M. Ferroni, C. Soldano, D. Zappa, V. Ferrari, G. Sberveglieri, *Seebeck effect in ZnO nanowires for micropower generation*, Procedia Engineering, 25, (2011), 1481-1484.

[8] E. Comini, *Metal oxide nano-crystals for gas sensing*, Analytica Chimica Acta, 568, 1-2, (2006), 28-40.

[9] D. Zappa, E. Comini, R. Zamani, J. Arbiol, J.R. Morante, G. Sberveglieri, *Copper oxide nanowires prepared by thermal oxidation for chemical sensing*, Procedia Engineering, 25, (2011), 753-756.